

In contrast to nitrogen, which constitutes 79% of the earth's atmosphere, phosphorus is present as mineral deposits, which are a nonrenewable natural resource. There is global concern about the energy and costs involved in mining the phosphate rock and its transport to manufacturing sites, as well as in the manufacture of different fertilizers and their transport to farm fields and application to the crops. This problem is very real and serious for a large number of countries having few or no phosphate rock deposits to meet their phosphate needs. Mining phosphate minerals and spreading phosphate fertilizers over the landscape is not sustainable because phosphate mineral deposits are limited. This problem will have to be addressed by future generations.

Another contrast between nitrogen and phosphorus results from the fact that, while nitrogen is easily lost from the soil by various mechanisms such as ammonia volatilization, leaching, and denitrification, the bulk of the phosphorus remains where it is applied due to its immobilization by reaction with Ca, Fe, and Al ions present in soil solution. Thus soluble phosphate fertilizer compounds once applied in the field soon revert to less soluble or insoluble forms. Only 15 to 20% of the applied phosphorus fertilizer becomes available to the crop, and a still smaller fraction to the succeeding crops (residual effect). Efficient phosphorus management therefore could be quite complicated, especially on high P-fixing, tropical ultisols and oxisols.

9.1. SOIL PHOSPHORUS

Total phosphorus content of soils is generally less than that of total N or K: about one-tenth to one-fourth that of nitrogen and one-twentieth that of K (Brady, 1990). Total P content in surface soil and subsoil may vary from a few mg kg⁻¹ to over 1 g kg⁻¹. Also in contrast to soil N, which is concentrated in surface soil, P content in subsoil may be less than, equal to, or greater than that in surface soil (Figure 9.1). The data in Figure 9.1 also show that P is present in soils both in organic and inorganic forms. Both organic and inorganic P continuously undergo transformation as shown in Figure 9.2.

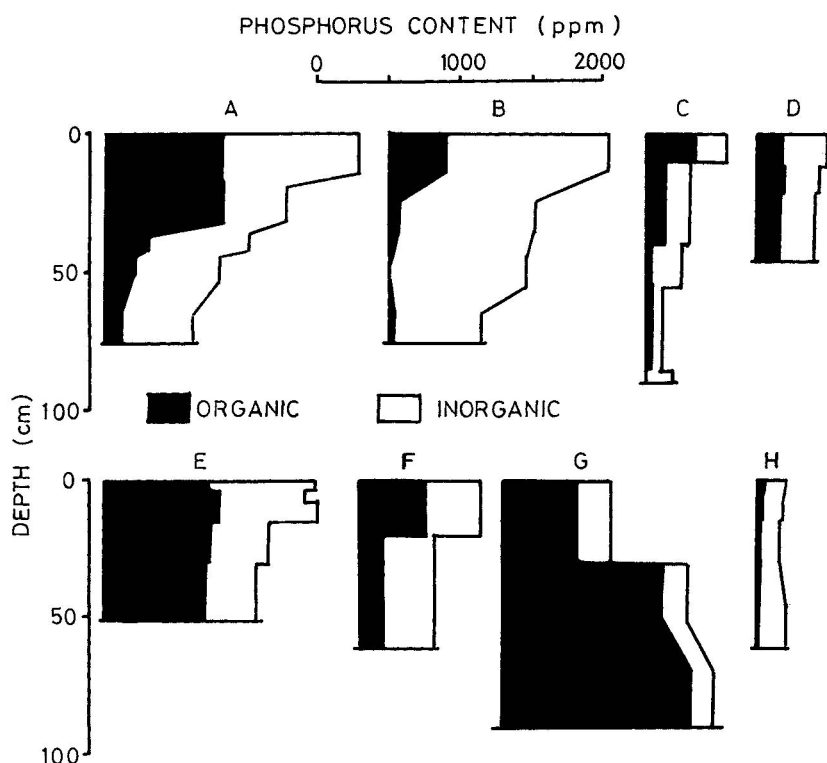


Figure 9.1. Distribution of phosphorus in various soil profiles. (From Anderson, G. 1986. *Phosphorus in Agriculture*, Khasawneh, F.E., Sample, E.C., and Kamprath, J.E., Eds. pp. 411–432. With permission of the Soil Scientific Society of America.)

9.1.1. Inorganic P

Inorganic P in soil is mostly present as compounds of Ca, Fe, and Al; Ca-phosphates dominate in neutral to alkaline soils, while Fe- and Al-phosphates dominate in acidic soils. At any specific time very small amounts of phosphate are present in soil solution in equilibrium with the solid inorganic phase. The concentration of P in soil solution is commonly approximately 0.05 mg l^{-1} and seldom exceeds 0.3 mg l^{-1} in unfertilized soils. When a water-soluble phosphate fertilizer such as super phosphate or ammonium phosphate is applied to soil, immediately after its dissolution the phosphate ions in solution react with Ca, Fe, or Al ions present in soil solution and are precipitated as insoluble compounds, or become adsorbed on the surface of clay particles. These processes are known as fixation or reversion of phosphate, and the compounds formed are known as “phosphate reaction products.” A discussion on these is provided in a later section of this chapter.

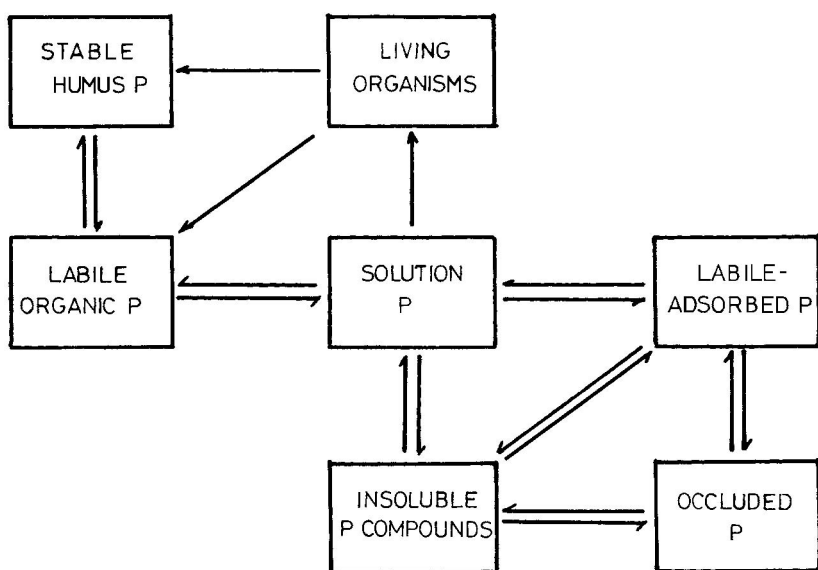


Figure 9.2. Phosphorus transformations in soil. (From Fixen and Grove, 1990. *Soil Testing and Plant Analysis*, Westerman, R.L., Ed. pp.141–180. With permission of Soil Scientific Society of America.)

The ionic forms of inorganic P are pH dependent, as shown in [Figure 9.3](#). Between pH values of 4.0 and 6.0, most of the P in soil solution is present as the H_2PO_4^- ion, the form in which it can be readily absorbed by plant roots because this ionic form is soluble in water. Between pH 6.5 and 7.5, P in soil solution is present partly as the H_2PO_4^- and partly as the HPO_4^{2-} ion. HPO_4^{2-} ions can also be taken up by the plant roots but not as readily as H_2PO_4^- ions. Between pH 8.0 and 10.0 the HPO_4^{2-} ion is dominant. Under such conditions Na^+ ions dominate the soil cation exchange complex, and some phosphate is present as sodium phosphate, making $\text{H}_2\text{PO}_4^{2-}$ ions available on hydrolysis. Beyond pH 10.0 the dominant ionic form of P is PO_4^{3+} , and unless present as sodium phosphate, P is not available to crop plants. At the other extreme, that is, below pH 3.0, which is generally not found in cultivated soils, P would be present in H_3PO_4 (phosphoric acid) form, a very reactive form. That is why in highly acidic ultisols and oxisols, phosphate fixation or reversion is rapid and large amounts of phosphate fertilizers are required to obtain good crop growth.

9.1.2. Organic P

The amount of P present in organic form in soils varies from a few milligrams to about 0.5 g kg⁻¹ soil (20 to 80% total P) (Figure 9.1). Organic P content depends upon a number of factors such as climate, vegetation, soil

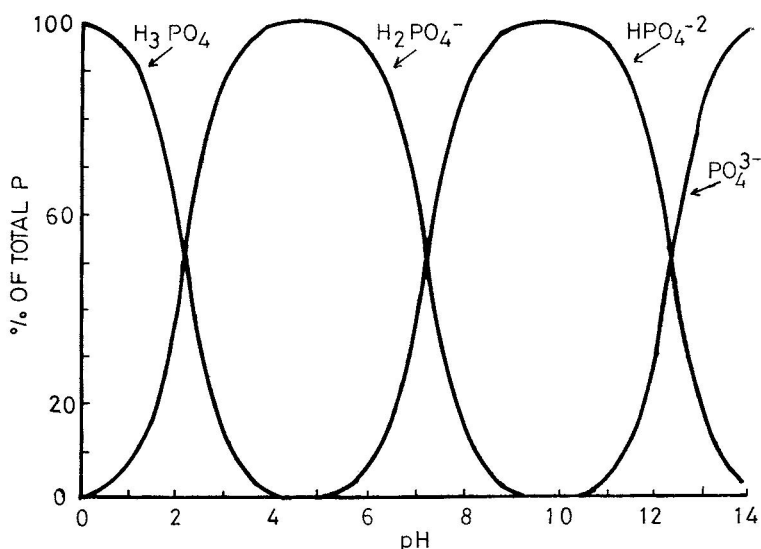


Figure 9.3. Distribution of orthophosphate species in solution as a function of pH.

texture, land use pattern, fertilizer practices, drainage and irrigation, etc.; a number of these factors are interdependent. In general, organic P in surface soils is a smaller fraction of total soil P in the warm regions than it is in the cool regions of the world; about 35.2% as organic P in equatorial regions (countries between 40° parallels) and 48.6% in colder regions (Harrison, 1987). Also more soil P is present as organic P in organic soils and peats (Histosols) than in mineral soils (Table 9.1). Again in mineral soils, high clay soils have a greater percentage of their P in organic form than do sandy soils. In general, organic P tends to accumulate in surface soil because organic P is a part of soil organic matter. However, there are soils such as uncultivated pine bogs where the subsoil is richer in P than the surface soil (Figure 9.1).

In the initial phase of pedogenesis most P in rocks is present as apatite (Figure 9.4), which is gradually brought into solution by chemical and biological processes. The P coming into soil solution is then reprecipitated as secondary inorganic phosphates or is utilized by microorganisms and plants, which after their death and decomposition make organic P available. Thus as pedogenesis proceeds, organic P accumulates. However, in the advanced stages of pedogenesis, when the bulk of the bases and silica has leached out (as in ultisols or oxisols) and soil mineral matter is dominated by Fe- and Al-hydroxides and oxyhydroxides, Fe- and Al-phosphates are formed and are precipitated. If Fe- or Al-hydroxides are precipitated on the surface of Fe- and Al-phosphates, the phosphate becomes occluded. Soils in the advanced stages of pedogenesis may contain sizable amounts of occluded secondary inorganic phosphate. Amount of organic P in such soils is considerably reduced. Ultisols

Table 9.1 Organic P Content of Surface Mineral/Organic Soils in Relation to Soil Texture

Soil texture	Number of samples	Organic P	
		(mg kg ⁻¹) Soil	% of total P
Mineral soils			
Sands	194	121	34.1
Loams	663	250	39.9
Clay loams and clays	309	332	41.4
Organic soils			
Organic loams	5	523	58.9
Peats	85	579	65.4

Adapted from Harrison (1987).

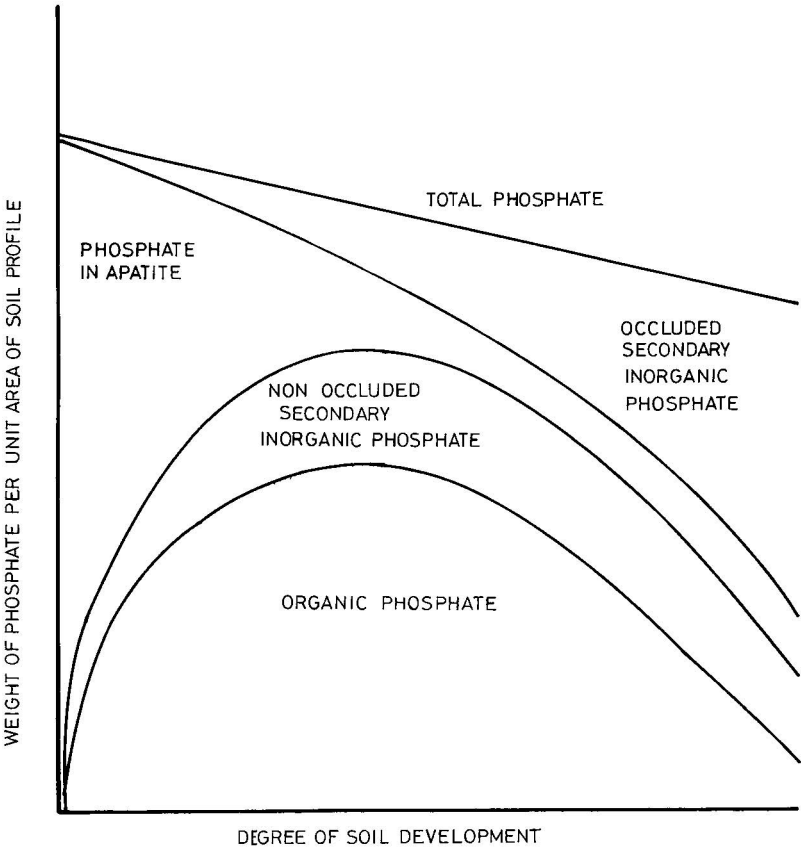


Figure 9.4. Changes in the magnitudes of phosphate fractions during pedogenesis. (From Williams and Walker, 1969. Soil Sci. 107:213–219. With permission of Williams & Wilkins.)

Table 9.2 Forms of Organic P in Soils

Form	Soil (mg kg ⁻¹)	% of organic P
Inositol phosphate	1.4–356	0.3–62
Nucleic acids	0.1–97	0.1–65
Phospholipids	0.4–17	0.03–5.4

Adapted from Harrison (1987).

and oxisols are found in warm regions of the world and in many cases organic matter content itself is very low, thereby reducing the organic P in soil.

Although often present in appreciable amounts, soil organic P has not been as intensively investigated as inorganic P. Three groups of organic-P compounds have so far been identified. These are inositol phosphates (phosphate esters of inositol C₆H₆(OH)₆), nucleic acids, and phospholipids. Together these forms may account for 50 to 70% of soil organic P (Table 9.2).

Inositol phosphate. Inositol phosphate is thought to be of microbial origin and can exist in several stereoisomeric forms; phosphate esters of myo-, scyllo-, neo-, and chrio-inositol have been characterized in soil (Cosgrove, 1962). Myo-inositol hexophosphoric acid (phytic acid) is usually a major pool of organic P. It is fairly stable in an alkaline medium, but gradually hydrolyzes to a range of intermediate inositol phosphates and finally to inositol in acidic media, the optimum for hydrolysis being near pH 4.0. Enzymes phytases also hydrolyze myo-inositol phosphates. Inositol phosphates make up from less than 1 to 62% of total organic P in soil (Table 9.2). In a wide range of soils from the United States, Canada, and Australia, inositol phosphates account for less than 20% of the organic P.

Nucleic acids. RNA (ribonucleic acid) and DNA (deoxyribonucleic acid) are found in all living beings. For a time it was believed that at least half of the organic P in soils was present in nucleic acids, but when specific methods of identification and measurements were applied, much lower values were found. For example, in the fulvic acid fraction of two Iowa soils not more than 1.2 to 6 mg P kg⁻¹ was present as nucleic acids; this was equivalent to 0.2 to 1.8% of the organic P. Harrison (1987), after surveying the world literature, reported values of 0.1 to 97 mg P kg⁻¹ as nucleic acid (0.1 to 65% of organic P); very high values should, however, be taken with caution.

Phospholipids. Most reported values of soil phospholipids fall within the range of 0.2 to 14 mg P kg⁻¹ soil (Kowalenko and McKercher, 1971) representing less than 5% of the organic P (also see Table 9.2). Phosphatidyl choline (lecithin) and phosphatidyl ethanolamine are the predominant phospholipids in soil.

Microorganisms are probably the major source of much of the remainder of the organic P (30 to 50%) in soils. Mention may be made of teichoic acids found in the cell walls of Gram-positive bacteria and of phosphorylated carboxylic acids other than uronic acid isolated from a number of Scottish soils.

Regarding the role of organic P in crop production, opinions differ; indeed some of the most P-deficient soils contain large amounts of organic P. Nevertheless, the importance of mineralization of organic P in the replenishment of P available to plants has frequently been well demonstrated. In soils with high organic matter content, only a small amount of organic P in soils needs to be mineralized to provide a substantial proportion of the P requirements of crops or natural vegetation.

9.2. PHOSPHATE RETENTION OR FIXATION IN SOIL

P is highly immobile in soils (Table 9.3) and generally is fixed near the point of application. To explain P fixation in soil, a wide variety of sorption and precipitation mechanisms has been suggested, with no real consensus as to the relative magnitudes of their contributions. Researchers using dilute P solutions, usually in the millimolar range, have developed several adsorption equations, while those working with concentrated P solution, usually in the molar range, have observed precipitates forming separately at the surfaces of soil constituents. There are four steps in the precipitation process that occurs when dissolved P reacts with soil: (1) formation of a surface-adsorbed P complex; (2) dissolution of clay minerals, which increases the P-reactive metal ion concentration in solution; (3) slow desorption of surface-adsorbed P compounds; and (4) slow nucleation, crystallization, and recrystallization of P compounds (Talibuddin, 1981). If the P retention processes are viewed throughout the entire zone influenced by fertilizer application and over an entire growing season or even a longer period, P retention in soil should be considered as a continuum embodying precipitation, chemisorption, and adsorption (Sample et al., 1986). Phosphorus is retained in soils by hydroxides and oxyhydroxides of Fe and Al, alumino-silicate minerals, soil carbonates, and soil organic matter.

9.2.1. P Retention by Hydroxides and Oxyhydroxides of Fe and Al

Retention of P by interaction with hydroxides and oxyhydroxides of Fe and Al in dilute solutions of P involves replacement of OH^- by PO_4^{3-} . One or both the hydroxyls may be involved. When only one hydroxyl is involved, the adsorption is said to be reversible (Figure 9.5), and when two hydroxyls are involved, the adsorption is said to be irreversible (Hingston et al., 1974). The other terms used for P adsorption involving two hydroxyls are bidentate and binucleate fixation of P. Surface complexes between Al^{3+} and phosphate are more labile than those involving Fe^{3+} . Furthermore, noncrystalline Fe-oxides, which have surface areas of $400 \text{ m}^2 \text{ g}^{-1}$, may play a wider role than the

Table 9.3 Extent of Movement of Phosphate Solution^{a,b}

Cumulative time (hr)	Thickness (mm) of the wetted soil shell		Thickness (mm) of drained time DCP shell in tablet	
	Moisture equivalent			
	0.5	1.0	0.5	1.0
2	1.0	1.0	0.5	0.5
18	2.2	2.0	1.0	0.9
44	3.7	3.1	2.0	1.1
69	4.5	3.3	2.3	1.3
164	5.4	3.5	4.0	3.0
216	5.4	3.5	4.0	3.0

^a Recrystallized monocalcium phosphate monohydrate (MCP). Reagent grade was compressed to tablets of 3 mm in thickness and 8 mm in diameter and contained 0.1 g of P. Tablets were inserted to a depth of 2.54 cm in 100-g soil samples (wetted to 0.5 or 1.0 ME [moisture equivalent] and loaded into a glass cell), and the cell was sealed promptly. Microscopic observations were then made.

^b Means of five soils.

Adapted from Lehr et al. (1959).

crystalline Fe-oxides, which have a surface area of about $100 \text{ m}^2 \text{ g}^{-1}$. Different Fe-oxides can have widely different P sorption capacities. For example, synthetic hematite could adsorb only $0.2 \mu\text{mol P m}^{-2}$, while synthetic goethites are reported to adsorb around $2.5 \mu\text{mol P m}^{-2}$.

One of the consequences of the specific adsorption of phosphate or other anions by Fe- and Al-hydroxides and oxyhydroxides is an increase in the negative charge (CEC). For example, Nakaru and Uehara (1972) reported that P adsorption increased the CEC of ferruginous tropical soils up to 100 cmol kg^{-1} ; the ratio of change being approximately 0.8 cmol/cmol of P added. Schalscha et al. (1974) demonstrated that CEC of some volcanic soils as determined with KH_2PO_4 was much greater than that with KCl or NaCl and that P adsorption increased the CEC.

9.2.2. P Retention by Clay Minerals

As with Fe- and Al-hydroxides, several researchers invoke a low-concentration sorption and high-concentration precipitation mechanism. With low P concentrations reactions with silicate minerals are much slower than with Fe- and Al-hydroxides. The edge faces of kaolinite (have OH^-) behave similar to the Al-hydroxides in the adsorption of P (Hingston et al., 1972). The P adsorption capacity by clay minerals depends, among other factors, on the proportion of surface area occupied by edge faces. Accordingly, kaolinite adsorbs more P per unit surface area than 2:1 clay minerals.

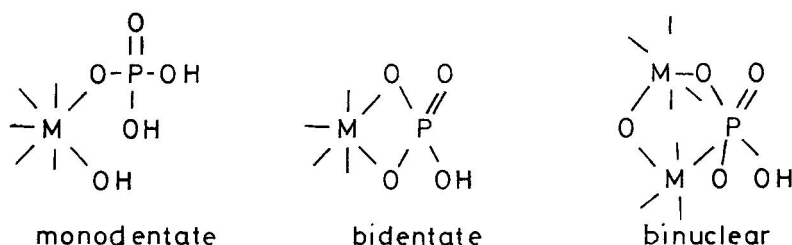


Figure 9.5. Reversible (monodentate) and irreversible (bidentate and binuclear) adsorption of P. (From Hingston et al., 1974; Fixen and Grove, 1990.)

With strong P solutions such as 1 M (ammonium, potassium, and sodium phosphate) illite, kaolinite, and monmorillonite behave the same way as Fe- and Al-hydroxides and oxyhydroxides and give precipitated phases consisting of Fe- and Al-phosphates containing the cations furnished by the P solution. Also concentrated P solutions decompose kaolinite (Kittrick and Jackson, 1956), resulting in precipitation of an Al-P compound. Lindsay and Stephenson (1959) reacted successive increments of Hartsells FSL (fine, sandy loam) (pH 4.6, from Tennessee) and Rosebud loam (pH 7.6, from Nebraska) with a triple-point solution TPS (the solution in equilibrium with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and CaHPO_4 ; the most concentrated solution resulting from the dissolution of mono-calcium phosphate in water having pH 1.01 and 4.50 M P and 1.34 M Ca). As successive soil increments were contacted by the TPS, simulating its movement from a fertilizer granule, the dissolution processes of Fe, Al, and Ca continued and the pH of the solution gradually increased (Figure 9.6), though it still remained strongly acid (pH 2 to 2.4). Soluble Fe and Al concentrations in both the soils continuously increased. With 1 hour contact time the concentration of soluble Fe in Hartsells FSL was 150 mmol l⁻¹ with ten increments of soil, the corresponding value for Rosebud loam was slightly more. Soluble Al concentration after 1 hour of contact with ten increments of soil was about 260 mmol l⁻¹ in Hartsell FSL and about 140 mmol l⁻¹ in Rosebud loam. Concentration of soluble Al increased with time of contact in both soils. However, for Fe, concentration decreased in Rosebud loam showing precipitation of Fe-phosphate. These data clearly show that fixation or retention of phosphate in soils involves dissolution and precipitation.

9.2.3. Retention by Soil Carbonates

The chemistry of calcareous soils is dominated by soil carbonates. Thus reactions of P with pure carbonates have been studied in some detail. P interactions with calcite involve two reactions: the first reaction at low P concentrations consists of adsorption of P by calcite surface, while the second process is a nucleation process of calcium phosphate crystals (Griffin and

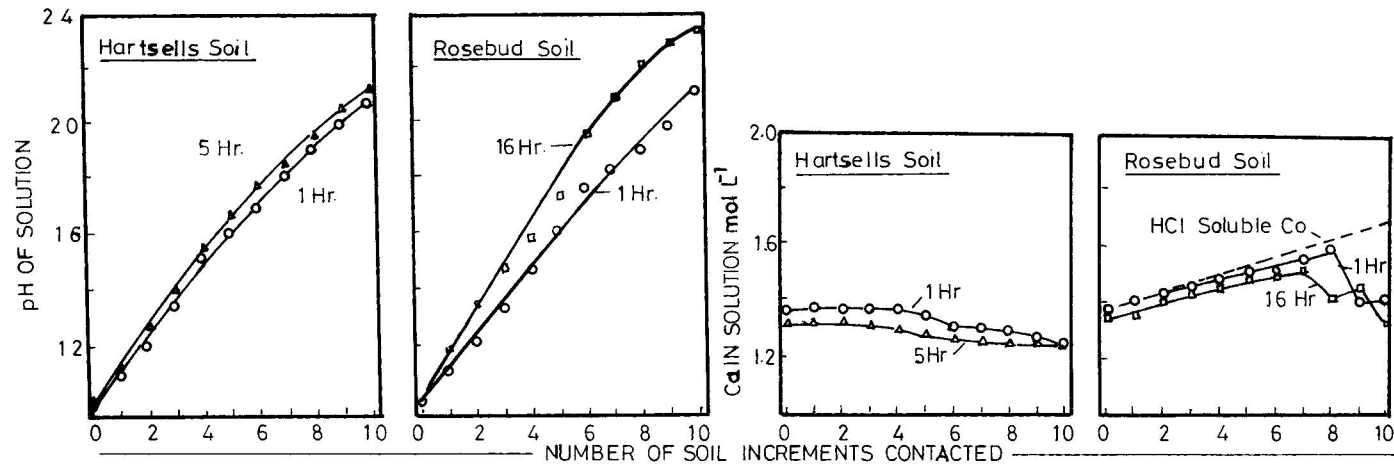


Figure 9.6. Soil pH, Ca, Fe, and Al concentration in solution brought about by bringing successive increments of soil in contact with a triple-point solution. (Adapted from Lindsay and Stephenson, 1959.)

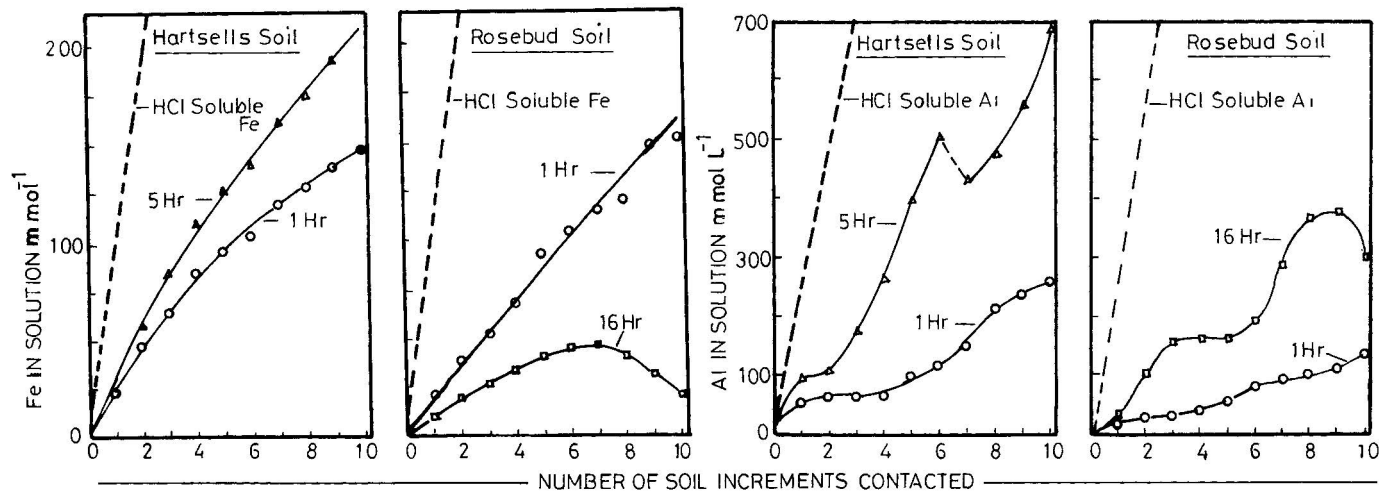


Figure 9.6. (Continued)

Jurinak, 1973, 1974). At high P concentrations, precipitation reactions are both copious and rapid. There is evidence to suggest that P is less strongly bound to CaCO_3 than to the hydrous oxides of Fe and Al and hence is more available to crop plants. The general consensus is that in soils where Al- and Fe-oxide are available, carbonates may play only a secondary role in P sorption. However, in soils where Fe-oxide and clay contents are very low, such as in some calcareous Vertisols and soils of arid regions, carbonates have a major effect on P solubility.

9.2.4. Retention by Soil Organic Matter

Soil organic matter is involved in retention and release of P. In association with cations such as Fe, Al, and Ca soil humus is able to retain significant amounts of P. On the other hand, researchers working with dilute P solutions have shown that organic matter complexes Ca, Fe, and Al and therefore makes more P available to plants.

When fertilizer P is applied to soils, organic matter coatings in the microsite are dissolved and move with the advancing front of the fertilizer. Giordano et al. (1971) showed that up to 10% of the soil organic matter was dissolved by mono-ammonium phosphate (MAP) and ammonium pyrophosphate (APP); APP dissolved twice as much as MAP. Removal of organic matter coatings on soil minerals may expose new surfaces for P precipitation at the microsite of fertilizer granule application. On the other hand, the dissolved organic matter may be reprecipitated in P-retention reactions. Soil organic matter can thus change the site of P retention.

9.3. FACTORS AFFECTING THE RETENTION OF PHOSPHOROUS BY SOIL

In addition to the soil components directly involved in the retention of phosphorus in soils, namely, Fe- and Al-oxides, clay minerals, carbonates, and organic matter, a number of other soil factors may also affect P retention by soil. These are briefly discussed.

9.3.1. pH

Soil pH has a profound influence on the availability of Ca, Al, Fe, and other ions in soil solution and thus has an overriding influence on the retention of phosphorus by soil. Phosphorus availability (solubility) in soils is greatest in the pH range 6 to 6.5 (Figure 9.7). At lower pH, increased solubility of Fe and Al results in retention of applied P as Fe- and Al-phosphates, while at higher pH (above 7.0), Ca plays a dominant role in phosphate retention. Liming of acid soils increases the availability of phosphorus by decreasing P fixation. For example, in a study on an oxisol in Brazil (Table 9.4), response to P applied

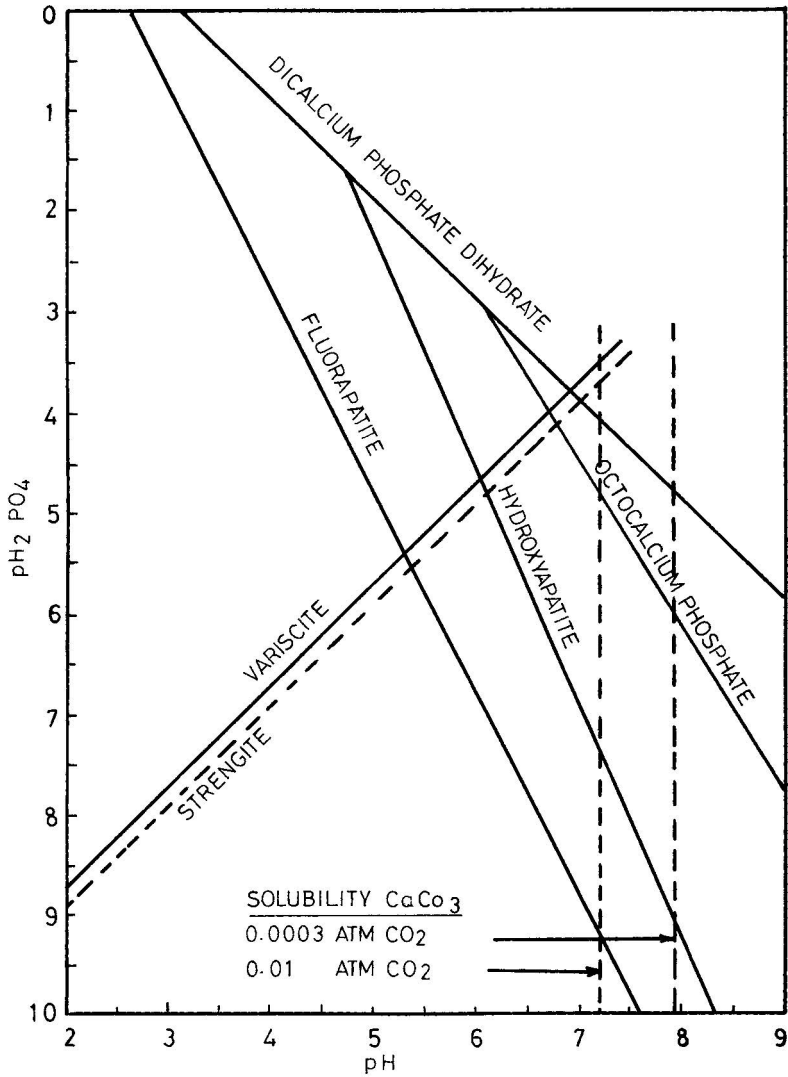


Figure 9.7. Solubility diagram for phosphate compounds in soils at 25°C and 0.005 M Ca concentrations (pCA = 2.50). (Adapted from Lindsay and Moreno, 1960.)

at lower rates was much greater in the presence of lime; but at higher levels of P application the effect of liming was not as apparent because the crop was able to meet its P requirements. In another study in Australia four times as much superphosphate was required to produce equal yields of alfalfa on a soil of pH 5.1 and 49% Al saturation as on a limed soil at pH 6.1 with no Al (Munns, 1965).

Table 9.4 Effect of Lime on Seed Yield (kg ha⁻¹) of Common Bean (*Phaseolus vulgaris* L.) Grown at Different P Rates in an Oxisol in Central Brazil

P level (kg ha⁻¹)	Without lime	With lime
0	37	110
26	777	900
52	953	1207
104	1427	1380
208	1323	1363

From Fageria et al. 1990. *Crops and Enhancers of Nutrient Use*, Baligar, V.C. and Duncan, R.R., Eds., p. 675. With permission of Academic Press.

9.3.2. Cations Present in Soil Solution

In addition to Fe, Al, and Ca, which are directly involved in phosphorus retention, presence of other cations can also influence the retention of phosphorus by soil. For example, Mg has been shown to prevent adsorption of phosphate onto calcite (Yadav et al., 1984). In sodic soils, where Na ions play a dominant role, phosphorus becomes associated with Na and is readily available to plants, resulting in a net reduction in the retention of soil phosphorus.

9.3.3. Anion Effects

Specifically sorbed ions such as hydroxyl, sulfate, and molybdate can compete with phosphate for the available reaction sites; nevertheless, phosphate is a stronger competitor.

9.3.4. Temperature

An increase in temperature generally decreases the availability of inorganic P. A study at the Northern Plains Field Station at Mandan, North Dakota, (Power et al., 1964) showed that both the water and NaHCO₃-extractable P extracted from soils to which phosphate fertilizer had been added decreased when the soil incubation temperatures were above 15°C. Beaton et al. (1965) reported that there was a 33% reduction in water-soluble phosphorus for each 15°C increase in temperature. This corollary explains why soils in warm regions of the world are generally much greater fixers of phosphorus than the soils of cooler regions. On the other hand, mineralization of phosphorus from soil organic matter or crop residues generally increases with an increase in soil temperature. For example, Campbell et al. (1984) from a 12-year study in Saskatchewan reported that the bicarbonate-soluble P increased between late fall and spring thaw.

9.4. PHOSPHATE FERTILIZER REACTION PRODUCTS IN SOIL

Even under conditions of low soil water, dissolution of phosphate granules containing water-soluble P is fairly rapid. For example, Lawton and Vomocil (1954) found that the water content of ordinary superphosphate granules in a soil at more than 1.5 MPa water tension increased to 16.2% within 24 hours. Thus ample water had diffused into the granules to initiate dissolution.

Once the saturated solution in and around the fertilizer granule or band is formed, an osmotic potential gradient is established between the concentrated fertilizer solution and the soil water. Water is drawn into this concentrated zone by vapor transport; the more the inward movement of water, the more is outward movement of solution. As long as the original salt remains, this process continues to produce a nearly saturated solution until the concentration is decreased by dilution or by reaction of fertilizer and soil constituents or until the osmotic gradient disappears. This phenomenon is also true for fertilizer materials of low-water solubility such as dicalcium phosphate and apatites, with the only difference being that the saturated solutions are more dilute (as dictated by the solubility products of the chemical compounds) and create a very small osmotic gradient between the fertilizer solution and soil solution. The chemical environments near the application of fluid fertilizers are quite similar to those surrounding highly water-soluble, solid fertilizers.

The solubility product (SP) principle has been widely used in identifying the phosphate reaction products, and a brief discussion follows. The SP principle applies to chemical compounds, which are sparingly soluble, for example BaSO_4 . When a small quantity of BaSO_4 is placed in water, despite the sparingly soluble characteristic of the compound, very low activities of Ba (A_{Ba}) and SO_4 (A_{SO_4}) can be measured in the water. The product of the activities of Ba and SO_4 ($A_{\text{Ba}} \times A_{\text{SO}_4}$), symbolized as $\text{SP}_{\text{BaSO}_4}$, has been found to be constant, irrespective of the source of BaSO_4 . The term pK SP is defined as

$\log \left(\frac{1}{\text{SP}} \right)$ following the terminology for pH. pK_{sp} values for such sparingly soluble compounds have therefore been used to identify unknown substances by matching the values obtained with those of the known compounds. Since many phosphate reaction products are sparingly soluble, this technique has been used in the identification of some of these compounds (Lindsay et al., 1959; Wright and Peach, 1980). pK_{sp} values for some phosphate compounds and stable forms of Fe, Al, and Ca (the ions that react with phosphate in soil solution) are given in Table 9.5.

Phosphate in soil solution is in a dynamic state and is continuously reacting with Ca, Fe, and Al. The rate of reaction depends on soil pH and the activity of reacting cations. Phosphate reaction products are essentially different phases in an overall reactive and dynamic state of soil solution. The phosphate phase present at a particular point can be predicted by using phase

Table 9.5 Solubility Expressions and Solubility Products of Some Phosphate Compounds at 25°C

Compound or species	Chemical formula	Solubility expression when activity of $H_2O = 1$	pK _{sp}
Gibbsite	$Al(OH)_3$	$pK_g = pAl + 3pOH$	33.8
Variscite	$Al(OH)H_2PO_4^a$	$pK_v = pAl + 2pOH + pH_2PO_4$	30.5
Goethite	$FeOOH$	$pK_{gt} = pFe + 3pOH$	unknown
Ferric hydroxide	$FeOOH$	$pK_{fh} = pFe + 3pOH$	38.1
Strengite	$Fe(OH)_2H_2PO_4^a$	$pK_{st} = pFe + 2pOH + pH_2PO_4$	33.6–35.0
Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	$pK_{dcpd} = pCa + pHPO_4$	6.56
Dicalcium phosphate anhydrous	$CaHPO_4$	$pK_{dcpa} = pCa + pHPO_4$	6.66
Octocalcium phosphate	$Ca_4H(PO_4)_3 \cdot 3H_2O$	$pK_{ocp} = 4pCa + pH + 3pPO_4$	46.91
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	$pK_{ha} = 10pCa + 6pPO_4 + 2pOH$	113.7
Fluorapatite	$Ca_{10}(PO_4)_6F_2$	$pK_{fa} = 10pCa + 6pPO_4 + 2pF$	118.4
Fluorite	CaF_2	$pK_{ft} = pCa + 2pF$	9.84
Calcite	$CaCO_3$	$pK_{cc} = pH - 1/2 pCa + 1/2 \log pCO_2$	4.93
Phosphoric acid	H_3PO_4	$pK_1 = pH + pH_2PO_4 - pH_3PO_4$	2.12
Dihydrogen phosphate ion	$H_2PO_4^-$	$pK_2 = pH + pHPO_4 - pH_2PO_4$	7.20
Monohydrogen phosphate ion	HPO_4^-	$pK_3 = pH + pPO_4 - pHPO_4$	12.32

^a The chemical formulate for variscite and strengite may also be expressed as $AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$, respectively.

Adapted from Lindsay and Moreno (1960).

diagrams such as the one shown in Figure 9.7. In Figure 9.7 lines represent the activity solubility isotherms for the respective phosphate compounds. Points falling above these isotherms represent supersaturation of the soil solution with respect to that compound, indicating that that compound is likely to be precipitated. Since in calcareous soils pH is governed predominantly by the solubility of CaCO_3 and the partial pressure of CO_2 , pH values are indicated in Figure 9.7 at two partial pressures of CO_2 by broken vertical lines for the value $p\text{Ca} = 2.5$.

The best documented example of P-reaction products is the dicalcium phosphate (DCP) residues remaining at application sites of fertilizers containing monocalcium phosphate (MCP). For example when MCP, OSP (ordinary superphosphate), or CSP (concentrated superphosphate) granules were placed in five soils at two water levels, 20 to 34% of the applied P remained as DCP after complete dissolution of the MCP component (Lehr et al., 1959). Dicalcium phosphate dihydrate (DCPD) is the dominant initial reaction product of these fertilizers, with monocalcium phosphate (MCP), formed in most alkaline and calcareous soils.

The reactions products and their amounts resulting from fertilizer mixtures are reported to be different than those from the pure phosphate fertilizers. For example, Bouldin et al. (1960) placed granules containing MCP + $(\text{NH}_4)_2 \text{SO}_4$ in moist soil and found that only about 2% P remained as dicalcium phosphate anhydrate (DCPA) residue after 3 weeks as compared with 21% with MCP alone. Bouldin et al. (1960) reported the following sequence of reaction products from granules of MCP + KCl.

Time (hours)	Reaction Products
2	MCP and KCl bulk phases; $\text{Ca}_2\text{K H}_7 (\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ minor phase
17.5	KCl and $\text{Ca}_2\text{K H}_7 (\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ major phase; MCP and DCPD (dicalcium phosphate dihydrate) minor phase
21	$\text{Ca}_2\text{K H}_7 (\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ major phase; DCPD and KH_2PO_4 minor phases
23.5	DCPD major phase; Abundant $\text{Ca}_2\text{K H}_7 (\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ and a trace of KH_2PO_4
25.5	DCPD major phase; $\text{Ca}_2\text{K H}_7 (\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ minor phase

With alkaline phosphate fertilizer DAP, MAP, and MCP, the products $\text{Ca}_8 \text{H}_2 (\text{PO}_4)_6 \cdot 5 \text{H}_2\text{O}$, $\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Mg NH}_4 \text{PO}_4 \cdot 6\text{H}_2\text{O}$ were identified in slightly acidic and calcareous soils (Bell and Black, 1970). With monoammonium (MAP) and monopotassium phosphate (MKP), ammonium taranakite and traces of variscite and potassium taranakite were the dominant products in an acidic soil from Tripura, while brushite, struvite, and newberryite with MAP and brushite and monetite with MKP were the main products on a calcareous alluvial soil from Bihar (Das and Datta, 1969). With monocalcium

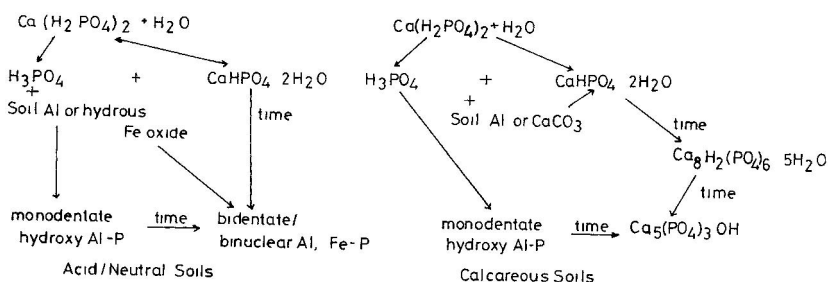


Figure 9.8. Transformations of monocalcium phosphate in soils. (Adapted from Thomas and Peaslee, 1973.)

phosphate there was considerable dissolution of Fe and Al, which precipitated as amorphous Fe- and Al-phosphates, in addition to brushite and monetite in both the soils (Das and Datta, 1969).

Lindsay et al. (1962) added soil and soil constituents to saturated solutions of the common fertilizers and identified 30 crystalline P compounds, in addition to colloidal precipitates of variable composition. In acidic soils the initial reaction products such as the taranakites and amorphous Fe- and Al phosphates, as well as calcium phosphates, change with time to variscite-like and strengite-like crystalline compounds.

With triammonium pyrophosphate (TPP), a major constituent of ammonium polyphosphate, in most Indian soils under study (alfisol, oxisol, entisol, mollisol, and vertisol) the most abundant products were $\text{Ca}(\text{NH}_4)_2 \text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and $\text{Mg}(\text{NH}_4)_2 \text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (Yadav and Mistry, 1984). Some other reaction products identified were $\text{Ca}(\text{NH}_4)_4 \text{H}_2(\text{P}_2\text{O}_7)_2$; $\text{Ca}_3(\text{NH}_4)_4 \text{H}_6 \text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$; $\text{Fe}(\text{NH}_4)_2 \text{P}_2\text{O}_7$; $\text{Ca}(\text{NH}_4)_2 \text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$; $\text{Mg}(\text{NH}_4)_2 \text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4 \text{Al}_{0.33} \text{Fe}_{0.67} \text{P}_2\text{O}_7$.

In nature the ultimate products are thought to be hydroxy and fluoroapatites in alkaline and calcareous soils and variscite and strengite in acidic to neutral soils (Hsu and Jackson, 1960). For ordinary or triple superphosphates containing monocalcium as the P compound, the transformations as given by Thomas and Peeslee (1973) are shown in Figure 9.8. As soil weathers with a decrease in pH, Ca-phosphates change to amorphous and crystalline Al-phosphates, which in turn change to Fe-phosphates (Chang and Jackson, 1958; Hsu and Jackson, 1960).

A summary of compounds formed from the reaction of phosphate fertilizers with soils and soil constituents is given in Table 9.6.

9.5. INTENSITY (I) AND QUANTITY (Q) FACTORS IN PHOSPHORUS AVAILABILITY

The quantity of P present in soil solution at a given time is a measure of its intensity. P concentration may be measured as molar concentration of total

Table 9.6 Summary of Compounds Formed from the Reaction of Phosphate Fertilizers with Soils or Soil Constituents

Compound	Mineral name	Compound	Mineral name
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	Variscite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Metastrengite
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	Metavariscite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Vivianite
$\text{Al}(\text{NH}_4)_2\text{H}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	—	$\text{FeNH}_4(\text{HPO}_4)_2$	—
$\text{Al}_2(\text{NH}_4)_2\text{H}_4(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$	—	$\text{Fe}_3\text{NH}_4\text{H}_6(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$	—
$\text{Al}_5(\text{NH}_4)_3\text{H}_6(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$	NH_4 -taranakite	$\text{Fe}_3\text{KH}_6(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$	—
$\text{AlNH}_4\text{PO}_4\text{OH} \cdot 2\text{H}_2\text{O}$	—	$\text{Fe}_2\text{K}(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	K-leucophosphite
$\text{AlNH}_4\text{PO}_4\text{OH} \cdot 3\text{H}_2\text{O}$	—	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Newberryite
$\text{Al}_2\text{NH}_4(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	—	$\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	—
$\text{Al}_2\text{NH}_4(\text{PO}_4)_2\text{OH} \cdot 8\text{H}_2\text{O}$	—	$\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$	—
$\text{AlKH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	—	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	Struvite
$\text{Al}_5\text{K}_3\text{H}_6(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$	K-taranakite	$\text{Mg}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$	Schertelite
$\text{Al}_2\text{K}(\text{PO}_4)_2\text{OH} \cdot 2\text{H}_2\text{O}$	Leucophosphite	$\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}$	Hannayite
$\text{AlKPO}_4\text{OH} \cdot 0.5\text{H}_2\text{O}$	—	$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	—
$\text{AlKPO}_4\text{OH} \cdot 1.5\text{H}_2\text{O}$	—	$\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$	—
$\text{Al}_2\text{K}(\text{PO}_4)_2(\text{F},\text{OH}) \cdot 3\text{H}_2\text{O}$	Minyulite	$\text{Al}(\text{NH}_4)_2\text{P}_2\text{O}_7\text{OH} \cdot 2\text{H}_2\text{O}$	—
CaHPO_4	Monetite	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	—
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Brushite	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	Octocalcium phosphate	$\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$	—

Table 9.6 Summary of Compounds Formed from the Reaction of Phosphate Fertilizers with Soils or Soil Constituents (Continued)

Compound	Mineral name	Compound	Mineral name
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Hydroxyapatite	$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$	—
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	Fluorapatite	$\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{CaAlH}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	—	$\text{Ca}_5(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$	—
$\text{CaAl}_6\text{H}_4(\text{PO}_4)_3 \cdot 20\text{H}_2\text{O}$	—	$\text{CaNH}_4\text{HP}_2\text{O}_7$	—
$\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$	—	$\text{Ca}_2\text{NH}_4\text{H}_3(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$	—
$\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	—	$\text{CaK}_2\text{P}_2\text{O}_7$	—
$\text{Ca}_2\text{NH}_4\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	NH_4 -Flatt's salt	$\text{Ca}_3\text{K}_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	—
$\text{Ca}_2(\text{NH}_4)_2(\text{HPO}_4)_3 \cdot 2\text{H}_2\text{O}$	—	$\text{Ca}_6\text{K}_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$	—
$\text{CaKPO}_4 \cdot \text{H}_2\text{O}$	—	$\text{Ca}_2\text{KH}_3(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$	—
$\text{CaK}_3\text{H}(\text{PO}_4)_2$	—	$\text{CaNa}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{Ca}_2\text{KH}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	K-Flatt's salt	$\text{Fe}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	—
$\text{CaFe}_2\text{H}_4(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	—	$\text{Mg}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$	—
$\text{CaFe}_2\text{H}_4(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$	—	$\text{Mg}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	—
$\text{Ca}_3\text{Mg}_3(\text{PO}_4)_4$	—	$\text{Mg}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	—
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Strengite	$\text{Ca}(\text{NH}_4)_3\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$	—

From Sample et al., 1986. *The Role of Phosphorus in Agriculture*, Khasawneth, F.E., Sample, E.C., and Kamprath, E.J., Eds., p. 284. With permission of American Society of Agronomy.

soluble P, including all species of orthophosphate ions, as well as ion pairs in association with other cations. It may also be expressed in ppm or mg l^{-1} . The other terms used for intensity measurements are chemical potential of H_2PO_4 , and monocalcium phosphate potential (Schofield's phosphate potential).

When P intensity is diminished by withdrawal of P from solution, solid-phase P goes into solution to replenish the loss. The quantity of solid-phase P that acts as a reserve is called the "quantity factor"; some authors refer to it as the "capacity factor." However, the recent trend has been toward adopting the word "quantity" to describe these reserves and to assign "capacity" to gradients that relate quantity to intensity. The quantity factor or reserves of soil P refer to both the labile and non-labile forms of soil P (see [Figure 9.2](#)); the labile P is directly linked with solution P (intensity factor) with a high dissociation rate, while the nonlabile P is indirectly linked with solution P with a low dissociation rate. (Note the similarity between nonexchangeable and exchangeable components of the quantity factor of K and solution K — [Chapter 10](#).)

Basically, labile P is the fraction of soil P that is isotopically exchangeable with ^{32}P within a specified time (Olsen and Khasawneh, 1980). Isotopically exchangeable P, utilized by a growing plant over the span of a growing season, is called the L value. The E value is the laboratory equivalent of the L value, measured over a shorter but specified period of equilibration. These definitions clearly indicate that labile P does not present a precisely defined and a clearly distinct phase of solid-phase P, but one that has arbitrary boundaries of time and other procedural factors. For a general relationship between quantity (Q) and intensity (I) factors, the student is advised to read Chapter 10 on potassium.

Soil test extractants discussed in the next section tend to estimate the quantity factor. For a group of closely related soils, there would exist a certain degree of correlation between labile P and P extractable by different extractants, and it is this relationship that provides support for measuring the P quantity factor via chemical extractants.

9.6. SOIL TESTING FOR PHOSPHORUS

Soil testing for P is done using a chemical extractant. A large number of extractants have been suggested by various workers such as ammonium bicarbonate-DPTA, Brays 1 & 2, citric acid, bicarbonate-ammonium fluoride - EDTA, Mehlich I, II, and III, Morgan's acetic acid - sodium acetate, Olsen's 0.5 M sodium bicarbonate, and Truog's sulfuric acid - ammonium sulfate (Fixen and Grove, 1990). Surveys of procedures in use in the United States have indicated that Bray's P_1 , Mehlich III, and Olsen's extract are most often used. Bray's P_1 extract is $0.03 \text{ M NH}_4\text{F} + 0.025 \text{ M HCl}$, while Mehlich III is $0.015 \text{ M NH}_4\text{F} + 0.2 \text{ M CH}_3\text{COOH} + 0.25 \text{ M NH}_4\text{NO}_3 + 0.013 \text{ M HNO}_3$. Both these extractants are suited for acidic soils. Olsen's extracting solution is 0.5 M NaHCO_3 of pH 8.5 and is best suited for neutral, calcareous, and alkaline soils.

There are four general reactions contributing to P release from soil by different chemical extractants. These are (1) acid dissolution; (2) anion exchange; (3) cation complexation; and (4) cation hydrolysis. Chemical extractants containing acids such as Bray's P_1 or P_2 or Mehlich I, II, and III will dissolve soil P by acid dissolution. The solubility of soil phosphate in decreasing order is $Ca-P > Al-P > Fe-P$, Ca-P being the most soluble and Fe-P being the least soluble. Extractants containing bicarbonate, citrate, lactate, and sulfate can replace adsorbed soil P by anion exchange. Fluoride and certain organic anions (citrate and lactate) can complex Al, and extractants containing these anions can release P from Al-P compounds. Similarly, bicarbonate precipitates soluble Ca as $CaCO_3$, causing release of Ca-P. It is argued (Thomas and Peaslee 1973) that bicarbonate and F remove similar soil P forms, though F is more competitive/aggressive. Cation hydrolysis occurs at high pH values where the OH^- ions dissolve a portion of Al-P and Fe-P by hydrolysis of Al and Fe. Extractants containing HCO_3^- can extract some soil P by this process. The exact mechanism of release of P from soil organic compounds is not well understood, but the most successful extractant contains both fluoride and dilute acid. A knowledge of extractant-soil interaction chemistry is most useful when understanding divergent extractant behavior because of (1) differences in available P sources on soils of otherwise similar properties (Admont et al., 1986) or (2) differences among soils fertilized with a common P source (Varvel et al., 1981).

Another approach to available P assessment in soil is to use models. Models may or may not use extractable soil P. Barrow (1980) outlined a descriptive model that simulates the initially rapid, but ultimately slow, gradual decline in available P after fertilization while taking into account P removal by the harvested crop. A rather more mechanistic model on the same line was proposed by Wolf et al. (1987). Other proposed models such as those of Cox et al. (1981) and Jones et al. (1984) rely on soil test information. If models are to become more important in agronomic/environmental management (reducing reliance on conventional soil testing), more validation work needs to be done.

9.7. PHOSPHORUS-DEFICIENCY SYMPTOMS IN PLANTS

Phosphorus is readily mobilized in plants and when a deficiency occurs, the P contained in older tissues is transferred to the active meristematic region. Small leaves, darker green colored than normal with reddish purple cast and dying tips indicate P deficiency (Figure 9.9). Purpling in young plants is more distinct. Other symptoms in small grain crops such as wheat include stunted growth, poor tillering, and delayed maturity.

9.8. PHOSPHATE FERTILIZERS

All phosphate fertilizers are produced from phosphate rock; the only exceptions are polyphosphates produced from elemental P. Global phosphate



Figure 9.9. A young plant (above) and a stunted more mature plant (below) showing phosphorus deficiency. The leaves develop a purplish color. (From *Corn Field Manual*, J.R. Simplot Company, Minerals & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 2 following p. 170.

rock reserves are estimated at 41,000 million Mg. The countries having major reserves are Morocco (20,000 million Mg), former USSR (8000 million Mg), United States (5700 million Mg), Republic of South Africa (1800 million Mg), China (1000 million Mg), Western Sahara (850 million Mg), and Australia (800 million Mg) (Stowasser, 1979). Other countries important from the viewpoint of reserves of phosphate rock are Tunisia, Senegal, Algeria, Egypt, and Togo in Africa; Mexico; Brazil and Peru in South America; and Jordan and Syria in Asia.

Phosphate rock basically consists of fluor-, hydroxy-, chlor-, and carbonate apatites—fluoroapatite being the dominant mineral. Apatites have an insular structure, and therefore the phosphates they contain are not available to growing crop plants, unless the insular structure created by apatite bondage is broken down. This can be achieved by two ways, namely, reacting the phos-

phate rock with a strong acid such as sulfuric, nitric, hydrochloric, or phosphoric acid or by employing heat (very high temperatures, generally above 1400°C) and high pressure. When an acid is employed it disintegrates the mineral and its anionic component such as SO_4^{2-} , PO_4^{3-} , NO_3^- , or Cl^- reacts with calcium in the rock. When heat is employed, the fluoride, chloride, hydroxy, or carbonate ions present in the mineral are released as F, Cl, or CO_2 gases or water vapors, and the crystal structure of mineral is broken down. When finely ground rock phosphate is applied to acid soils, soil acids disintegrate the apatite minerals in the same way as strong acids, but the slower rate of reaction depends upon soil pH and potential acidity. Phosphate rock contains 11 to 16% P (25 to 37% P_2O_5) and 33 to 36% Ca. The most commonly manufactured and used phosphate fertilizers, along with their composition, are listed in Table 9.7, and a brief discussion of them follows.

9.8.1. Terminology

Phosphate in fertilizers may be present in one or more forms of orthophosphate ion (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , or condensed polyphosphates such as pry- and tripolyphosphate). Because these forms differ in their solubility, specific terms are used to define them.

9.8.1.1. Water-Soluble Phosphorus. A small sample of fertilizer is extracted with distilled water for a prescribed period (AOAC, 1960) and the slurry is then filtered. The amount of P in the filtrate is determined and expressed as a percentage by weight of the fertilizer. This fraction is called water-soluble P. Monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$], (the main P component of ordinary or concentrated phosphate), monoammonium phosphate [$\text{NH}_4\text{H}_2\text{PO}_4$], diammonium phosphate [$(\text{NH}_4)_2\text{HPO}_4$], and potassium phosphate [KH_2PO_4] are water soluble.

9.8.1.2. Citrate-Soluble Phosphorus. The fertilizer residue left after extracting water-soluble P is extracted with a neutral (pH 7.0) solution of 1 N ammonium citrate for a prescribed period (AOAC, 1960), and the slurry is then filtered. The phosphorus content in the filtrate is then determined and expressed as a percentage by weight of the fertilizer. This fraction is called citrate-soluble P. Some European countries use alkaline ammonium citrate solution for extracting phosphorus from fertilizers (Terman et al., 1964) in place of neutral ammonium citrate solution; alkaline extracting solution will extract lesser amounts of P (Figure 9.10) and is considered by some workers (Terman et al., 1964) to be better correlated with plant growth and P uptake. However, most countries in the world use neutral ammonium citrate solution for extracting citrate-soluble P.

Table 9.7 General Composition of Phosphate Fertilizers

Material	Total nitrogen (%)	Total potassium (%)	Total sulfur (%)	Total calcium (%)	Total magnesium (%)	Phosphorus	
						Total ^a (%)	Available ^b (% of total)
Ordinary superphosphate (OSP)	—	—	11–12	18–21	—	7–9.5	97–100
Conc. (triple) superphosphate (CSP)	—	—	0–1	12–14	—	19–23	96–99
Enriched superphosphate	—	—	7–9	16–18	—	11–13	96–99
Ammoniated OSP	2–5	—	10–72	17–21	—	6.1–8.7	96–98
Ammoniated CSP	4–6	—	0–1	12–14	—	19–21	96–99
Dicalcium phosphate	—	—	—	29	—	23	98
Ammonium phosphates ^c							
21-53-0	21	—	—	—	—	23	100
21-61-0	21	—	—	—	—	27	100
11-48-0	11	—	0–2	—	—	21	100
16-48-0	16	—	0–2	—	—	21	100
18-46-0	18	—	0–2	—	—	20	100
16-20-0	16	—	14	—	—	8.7	100

Table 9.7 General Composition of Phosphate Fertilizers (Continued)

Material	Total nitrogen (%)	Total potassium (%)	Total sulfur (%)	Total calcium (%)	Total magnesium (%)	Phosphorus	
						Total ^a (%)	Available ^b (% of total)
Ammonium phosphate nitrate	30	—	—	—	—	4	100
Ammonium polyphosphate	15	—	—	—	—	25	—
Potassium phosphate	—	29–45	—	—	—	18–22	100
Magnesium ammonium phosphate	8	—	—	—	—	14	17
Raw rock phosphate	—	—	—	33–36	—	11–17	14–65
Basic slag	—	—	0.2	32	3	3.5–8	62–94
Defluorinated phosphate rock	—	—	—	20	—	9	85
Phosphate rock-magnesium silicate	—	—	—	20	8.4	10	85
Rhenania phosphate	—	—	—	30	0.3	12	97
Potassium metaphosphate	—	29–32	—	—	—	24–25	—

^a Values given as elemental P. Fertilizers are generally marketed giving %P₂O₅, which can be obtained by multiplying P value with 2.27. For example, see the grades of ammonium phosphates in this table.

^b By neutral 1.0 N ammonium citrate procedure.

^c Ammonium phosphate grades expressed as %N, %P₂O₅, %K₂O.

From Tisdale et al., 1993. *Soil Fertility and Fertilizers*, 5th ed., p. 208. With permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

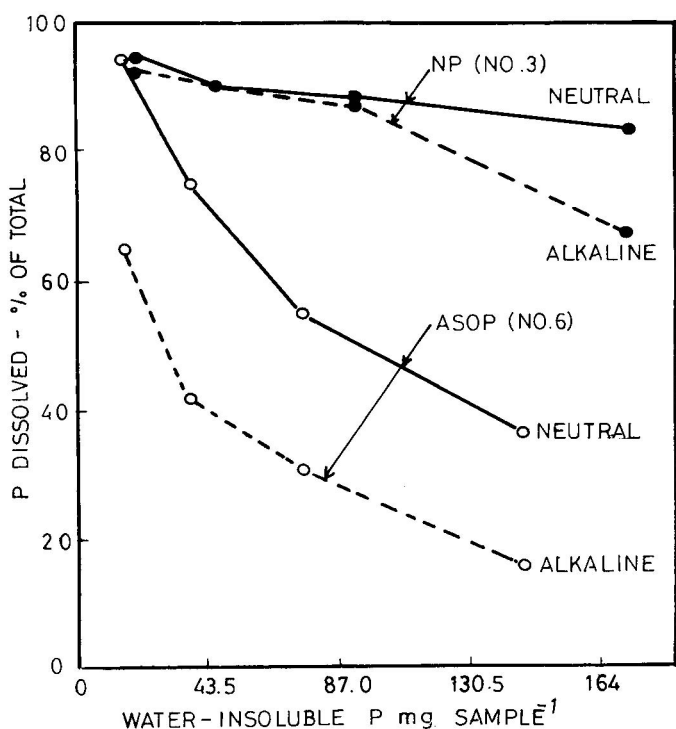


Figure 9.10. Water and citrate-soluble phosphorus in two fertilizer materials as affected by extraction with either neutral or alkaline ammonium citrate (From Terman et al., 1964. *Adv. Agron.* 16:59–100. With permission of Academic Press, Inc.)

9.8.1.3. Available Phosphorus. The sum of the water-soluble and citrate-soluble P represents an estimate of the fraction available to plants and is termed as available phosphorus.

9.8.1.4. Total Phosphorus. The sum of water-soluble, citrate-soluble, and citrate-insoluble P (P in residue left after extracting citrate-soluble P) represent the total P in fertilizer. Total P can be and is generally determined directly in a single step.

9.8.2. Phosphate Fertilizers

9.8.2.1. Ordinary (Single) Superphosphate

It is made by reacting phosphate rock with sulfuric acid and contains 7 to 9.5% P (16 to 22% P_2O_5) as monocalcium phosphate (MCP); about 90%

is water soluble. In addition, it contains 11 to 12% S as calcium sulfate. This material is ideally suited in areas where S is deficient.

9.8.2.2. Concentrated (Triple) Superphosphate

It is made by reacting phosphate rock with phosphoric acid and contains 19 to 23% P (44 to 52% P_2O_5) as MCP. All P present is water soluble.

9.8.2.3. Enriched Superphosphates

These are made by reacting phosphate rock with a mixture of sulfuric and phosphoric acids, and they contain 11 to 13% P (25 to 30% P_2O_5) of which 90 to 95% is water soluble.

9.8.2.4. Ammoniated Superphosphates

These are produced by reacting ordinary or triple superphosphate with anhydrous or aqua ammonia, and they contain 2 to 6% N and 6 to 21% P (14 to 49% P_2O_5). Ammoniation of superphosphate offers an inexpensive way of adding nitrogen to fertilizer, but reduces the water-soluble P content—less than 20% in ordinary superphosphate but nearly 50% in concentrated (triple) superphosphate (Terman et al., 1964). For crops responding to a high degree of water-soluble P, a high degree of ammoniation of ordinary superphosphate will have a depressing effect on the plant availability of P in fertilizer (Terman et al., 1964).

9.8.2.5. Ammonium Phosphates

These are made by reacting ammonia with phosphoric acid. Both monoammonium phosphate (MAP) and diammonium phosphate (DAP) are widely used. The common MAP grades vary from 11-48-0 (21% P) to 11-55-0 (26% P), while DAP grades are 16-48-0 (21% P), 18-46-0 (20% P), and 21-53-0 (23% P).

When sulfuric acid is mixed with phosphoric acid and ammoniation is done, the product is ammonium phosphate sulfate (16-20-0) (8.6% P). Similarly, urea can be added to DAP to obtain urea ammonium phosphate (28-28-0) (12.2% P).

9.8.2.6. Nitric or Nitrophosphates

These are made by reacting phosphate rock with nitric acid. Since one of the reaction products is calcium nitrate, which is highly hygroscopic, steps are taken to remove it or modify it to some other form. Calcium nitrate can be removed by refrigeration and centrifugation, or it can be converted to calcium carbonate by injecting carbon dioxide. Some processes employ the

use of sulfuric or phosphoric acid along with nitric acid to convert part of the calcium nitrate to calcium sulfate or calcium phosphate. The acidified slurry is then ammoniated. The final product contains a complex assortment of salts such as ammonium phosphate, dicalcium phosphate, ammonium nitrate, calcium sulfate, and others. The water solubility of nitric phosphates may vary from 0 to 80%, depending upon the process used. When used on crops responding to water-soluble P, nitric phosphates containing 30% or less water-soluble P may be inferior to P fertilizers containing a higher degree of water-soluble P (Prasad and Dixit, 1976). Nitric phosphates give best results on acidic soils and with crops with a relatively long growing season such as turf and sod crops (Tisdale et al., 1985) or sugarcane. Also when used in a cropping system and the study is extended to more than one crop, nitric phosphates may be as effective as highly water-soluble, P-containing fertilizers (Venugopalan and Prasad, 1989a).

9.8.2.7. Ammonium Polyphosphate

This product was developed by the Tennessee Valley Authority (TVA) in the United States by ammoniation of mixtures of electric-furnace superphosphoric acid and up to 30% of the P as wet-process orthophosphoric acid. This process results in a granular product with a grade of 15-62-0 (27% P). Both liquid and solid ammonium polyphosphate are available.

Before being taken up by plants, polyphosphates must undergo hydrolysis to change into orthophosphate; the hydrolysis is brought about by enzymes such as pryophosphatase (Dick and Tabatabai, 1986), which are generally present in soil. Venugopalan and Prasad (1989b) reported that the half-life values for the polyforms of P in liquid ammonium polyphosphate ranged between 1.6 to 2.0 days under anaerobic conditions and 5.2 to 8.7 days under aerobic conditions; the corresponding values for solid ammonium polyphosphate were 3.9 to 9.2 days under anaerobic and 12.5 to 27.0 under aerobic conditions. In this study the hydrolysis rate was fastest for a laterite, intermediate for a sodic, and slowest for an alluvial soil. Soil factors that may affect hydrolysis of ammonium polyphosphate are pH (greater hydrolysis on acidic than on alkaline soils), temperature (increases with a rise in temperature), texture, and water content (more hydrolysis on flooding).

In addition to high nutrient content, ammonium polyphosphates have the advantage of chelating micronutrients and reduced P-fixation due to the time required for their conversion to orthophosphates.

9.8.2.8. Thermal Phosphates

These fertilizers are made by the heat treatment of phosphate rock. There are two processes, namely, “calcination” and “fusion” by which thermal phosphates are made. In calcination the heating is done below the melting point

of the mixture, while in fusion it is done above the melting point, so that the material fuses together. The calcinated material is sintered and porous in appearance, while the fused material is a glossy product. Some important fertilizer materials in this group are as follows:

1. *Defluorinated phosphate rock or Coronet phosphate* is made by combining finely ground phosphate rock, high silica tailings from the phosphate rock mining process, and enough water to form a slurry. The slurry is passed into an oil-fired kiln having temperatures between 1480 to 1590°C and heated for 30 minutes. The product is then quenched and ground to allow 60% of it to pass a 200-mesh screen. It contains 9% total P (21% P_2O_5) out of which 8% P (18% P_2O_5) is citrate soluble.
2. *Rhenenia phosphate* is prepared by calcining a mixture of phosphate rock, soda ash, and silica at 1100 to 1200°C. It is then quenched and ground. It contains 12% total P (28% P_2O_5); 11.8% P (27.5% P_2O_5) is citrate soluble.
3. *Phosphate rock-magnesium silicate glass* is formed by fusing phosphate rock and olivine or serpentine in a furnace at 1550°C. It contains 10% total P (22.5% P_2O_5) - 8% P (19% P_2O_5) is citrate soluble.
4. *Basic or Thomas slag* is a by-product of the steel industry. Basic slag in the United States contains about 3% P_2O_5 , while that in Europe contains about 14 to 18% P_2O_5 . Indian basic slags contain 1.5 to 3% P_2O_5 .

The major disadvantages of thermal phosphates are (1) no water-soluble P; (2) high energy requirement for production, making it more expensive to produce; and (3) no value to the fertilizer industry because products cannot be ammoniated and thus manufacture of NPK fertilizers is not possible.

9.8.2.9. *Partially Acidulated Rock Phosphate (PARP)*

In countries where native S is not available and thus manufacture of sulfuric acid or phosphoric acid involves costs and foreign exchange, partial acidulation with sulfuric acid or other acids can be utilized. Generally, about half the quantity of acid is used. On a highly acidic and high P-fixing, dark-red latosol (oxisol), PARP was as good as triple superphosphate for rice and beans (Fageria et al., 1991). Sometimes PARPs may even perform better than ordinary or concentrated superphosphate (Marwaha, 1989). It is possible that the drop in pH in the soil surrounding a dissolving PARP granule is less than that around the fully acidulated fertilizer. In acidic soils this would result in less dissolution of Fe and Al and consequently less fixation of P; residues in the PARP granule and the reaction products in the soil may thus sustain a

higher solution-P concentration than for ordinary or concentrated superphosphate (Sharpley et al., 1992).

9.8.2.10. Rock Phosphate

Ground phosphate rock contains 11 to 16% total P (25 to 37% P_2O_5). As already discussed, most of the P is in apatite form and thus there is no water-soluble P. Citrate solubility can vary from 5 to 17% of the total P, depending upon the chemical nature of the rock and the degree to which it is ground. Direct application of finely ground phosphate is recommended for acidic soils (pH 6 or below). On highly acidic (pH 4.9) and high P-fixing, dark-red latosol (oxisol), ground Brazilian rock phosphates gave as good yields of rice and beans as triple superphosphate from the second year onward; in the first year there was very little response to ground-rock phosphate (this would be expected because soil acids solubilize rock-phosphate P rather slowly) (Fageria et al., 1991). In another study relative agronomic effectiveness (taking a value of 100% for concentrated superphosphate) ranged from 36 to 100% for ground (<0.075 mm) North Carolina phosphate rock (Chien and Friesen, 1992).

Thus phosphate fertilizers differ not only in their content of total P, but also in the form in which P is present. Choice of the fertilizer will depend upon the soil, the crop to be grown, and the price per unit of P.

9.9. EFFICIENT PHOSPHATE MANAGEMENT

Efficient phosphate management has three major components: (1) strategies for efficient utilization of native soil P; (2) strategies for efficient utilization of fertilizer P; and (3) strategies for the direct use of rock phosphate.

9.9.1. Strategies for Efficient Utilization of Native Soil P

9.9.1.1. Use of P-Efficient Crops and Their Cultivars

Crops and cultivars within crop species differ in their abilities to survive, grow, and produce at low levels of available P in soils. According to Loneragan (1978), the differences among plants in their ability to absorb P from soils may be due to at least three distinct root attributes: (1) the physiological ability to absorb P from dilute solutions; (2) metabolic activity resulting in solubilization of sorbed P; and (3) the ability of the root system to explore the soil mass. Plant species having deeper root systems can feed better on native soil P. Even within a crop, cultivars differ in their ability to feed and grow on native soil P. From a practical viewpoint, cultivars that produce well under a low level of P and respond well to added P are the most desirable. Fageria et al. (1988) screened 25 rice cultivars on an oxisol in Brazil and found that seven cultivars utilized P more efficiently than others.

9.9.1.2. Use of Vesicular Arbuscular Mycorrhizae (VAM)

The effect of mycorrhizae on increasing root extraction of P is well known for many species (Tinker, 1978; Kucey et al., 1989). Three primary mechanisms by which VAM enhance soil P utilization by plants are (1) the increased physical exploration of the soil; (2) chemical modification of the rhizosphere; and (3) physiological difference between VAM and plant roots (Sharpley et al., 1992; Gianinazzi-Pearson, 1986).

Extensive hyphal growth of VAM reduces the distance for diffusion of P in soil and thereby increases P uptake by plants. Furthermore, the smaller diameter of VAM hyphae (2 to 4 μm) compared with root hair (7 to 10 μm) affords a greater absorptive surface area for hyphae and enables the entry of hyphae into soil pores and organic matter that cannot be entered by root hairs.

VAM may chemically modify the rhizosphere through the exudation of chelating compounds or phosphatases, which help in solubilizing slowly soluble soil P.

Generally, the majority of work on the use of VAM has been done under controlled conditions. The use of these organisms to increase the availability of native soil P will much depend on the selection of strains that have the ability to increase P uptake and to compete with native soil microflora under natural conditions of crop production.

9.9.1.3. Use of Phosphobacterium

Bacterium *Bacillus megatherium* var. *phosphobacterium*, called a bio-fertilizer phosphobacterium (Cooper, 1959), was first used in the USSR for increasing the availability of native soil P. The bacteria was credited for mineralizing organic P in soils. In about 50% of the crops inoculated with this bacteria, yield increases of the order of 1 to 20% were obtained in Soviet soils. The best results were obtained on neutral to alkaline soils with high organic-matter content. A positive response to phosphobacterium has also been reported from India. However, no response was obtained in field tests with wheat, oats, and sorghum in Alaska, Minnesota, Montana, North Dakota, and Texas. There is a need to identify the soil and climatic conditions under which phosphobacterium can function.

9.9.2. Strategies for Efficient Utilization of Fertilizer Phosphorus

Due to the fast reactivity of soluble P in fertilizers with the cations in soil solution and cations and anions on the surface of clay and organic matter particles, P does not move far from the point of placement. Therefore the key to efficient P utilization is deep placement near the growing young roots of the crop (Figure 9.11). Although a few recommendations are available for foliar application of soluble phosphate fertilizers, most fertilizer phosphate is applied to soil before or at seeding of a crop. Deep placement in a standing

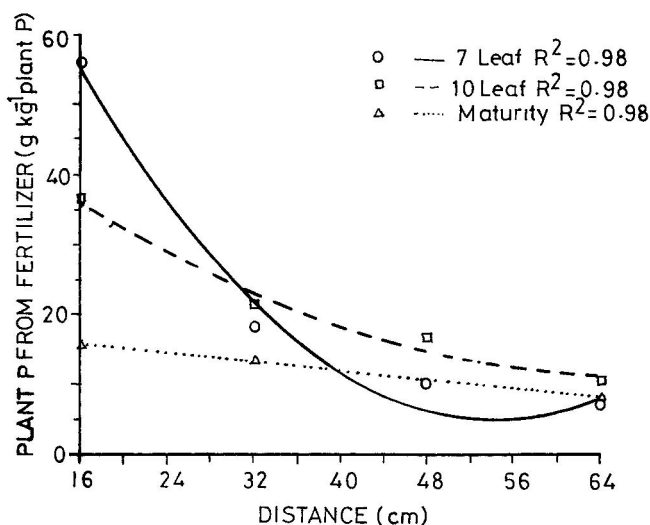


Figure 9.11. Effect of P distance from plants on P uptake from fertilizer at three sampling times over 2 years, 1984 and 1985. (From Eghball and Sander. 1989. Soil Sci. Soc. Am. J. 53:282–287. With permission of SSSA.)

crop without damaging the root system is neither possible nor desirable due to the immobile nature of P. However, in recent years some recommendations have emerged for split application of P in rice; top dressing in such cases has to be quite early in the crop's life span and can provide a solution in situations where phosphate fertilizers are not applied before transplanting.

A knowledge of the early rooting habits of various crop plants is helpful in determining the most satisfactory method of placing phosphate fertilizer. If a vigorous taproot is produced early, such as for cotton, tobacco, and most grain legumes, application may best be made directly under the seed. If many lateral roots are formed early, such as in cereals, side placement may be best. Increased root growth in the P-fertilized volume of soil compared with unfertilized soil is well known.

A rule of thumb is that, for row-sown crops, phosphate must be placed; the wider the interrow spacing, the greater the advantage of P placement. Only for those crops that are sown broadcast, incorporation in soil may be as good as deep placement. By banding, fertilizer P comes into less direct contact with soil, reducing the opportunity for fixation of soluble P. Likewise, using larger fertilizer P particles, which are subject to less fixation, is sometimes more effective than using finely ground P fertilizer.

In countries where rice is the principal crop, phosphate fertilizer is imported and expensive, and soils are usually high P-fixers. Dipping the rice seedlings before transplanting in a slurry of soil and phosphate fertilizer can increase the efficiency of fertilizer P and economize on phosphate use.

Table 9.8 Results of 3 Years of Experiments on Responses to P_2O_5 Application of Kharif^a and Rabi^b in Some Cropping Systems Involving Wheat

Cropping sequence	Research centre	Total rotational response to 60 kg P_2O_5 /ha	
		P_2O_5 applied to kharif crop (q/ha)	P_2O_5 applied to wheat crop (% change)
Rice-wheat	Raipur	13.4	+4
	Jabalpur	19.9	−6
	Kathulia	24.7	−26
	Bichpuri	13.0	−19
	Varanasi	6.7	−6
	Mashodha	11.9	+46
	Kharagpur	15.1	−53
Jowar-wheat	Indore	18.9	+1
	Siruguppa	25.5	+13
Maize-wheat	Palampur ^c	36.2	+17
	Ludhiana	14.2	+40
Bajra-wheat	Hissar	12.7	+6

^a Rainy season, July–October.

^b Fall–spring season, November–April.

^c At 120 kg P_2O_5 /ha.

From Goswami and Kamath. 1984. Fert. News 29(2):22–26.

In multiple cropping systems the recommendation is to give priority to those crops that are more responsive to P and are poor users of residual P (wheat, potato) as compared with crops that can benefit from residual P (rice, corn) (Goswami and Kamath, 1984) (Table 9.8).

9.9.3. Strategies for the Direct Use of Rock Phosphate

In general, rock phosphate can be directly used in acidic soils having pH below 5.5 to 6.0, but for this purpose the phosphate rock must be finely ground to assure an adequate rate of P release (Tisdale et al., 1985). Also, the dosages used with rock phosphate are generally several times those recommended for soluble P fertilizers (Kucey and Bole, 1984).

Plant species differ in the capacity to utilize P from rock phosphate. This may be related to cation exchange capacity (CEC) of roots; the higher the CEC, the greater the capacity to extract P from rock phosphate (Drake and Steckel, 1955). Also, a relationship has been observed between the rhizosphere pH and plant P uptake. For example, buckwheat (*Fayopyron esculentum* L.) can acidify its rhizosphere and cause dissolution of rock phosphate, but corn cannot.

Some of the strategies for increasing the efficiency of ground-rock phosphate are discussed as follows:

1. *Mixing rock phosphate with soluble P fertilizers.* It is possible to use finely ground rock phosphate at least in part mixed with soluble P fertilizers such as superphosphate. The proportion of the two materials will, of course, depend upon the soil conditions and the crop. Fageria et al. (1990) have also suggested the use of rock phosphate in combination with a soluble P source as a strategy for improving P status of acidic soils; they recommend broadcast application of rock phosphate and band application of soluble P sources.
2. *Mixing rock phosphate with elemental S or S-producing compounds.* Mixing of rock phosphate with elemental S was suggested in the early part of the century (Lipman et al., 1916) for increasing the availability of P in the rock. The principle involved is that the S in the mixture is oxidized to sulfuric acid by chemautotrophic bacteria (*Thiobacillus thiooxidans* and *Thiobacillus thioparus*), which solubilize the P in rock phosphate. This has been demonstrated on a number of soils. The availability of rock-phosphate-sulfur mixtures appears to be greatly influenced by a number of factors such as soil pH, soil temperature, soil water, and particle size of the mixture.

Swaby (1975) inoculated rock-phosphate-sulfur mixtures with *T. thiooxidans* and *T. thioparus* and called them biosupers; these mixtures were found to be superior to uninoculated mixtures for pasture production in tropical soils.

Iron pyrites as a source of sulfur have also been suggested for mixing with rock phosphate. This strategy has been used for utilizing low-analysis phosphate rock (18 to 20% P_2O_5), which cannot be used for making soluble phosphate fertilizers (Tiwari, 1979).

3. *Use of phosphate-solubilizing (PS) microorganisms.* The major site of occurrence of PS microorganisms has been on soil or seed surfaces. Phosphate-solubilizing organisms have been found in almost all soils tested, although the numbers vary with soil, climate, and cropping history (Chhonkar and Subba-Rao, 1967; Kucey, 1983). However, after subculturing PS isolates, many of the bacterial isolates may lose their PS activity. In several greenhouse studies, P uptake by inoculated plants was equal to or greater than that from superphosphate.

Several studies of PS microorganisms have also included the effect of VA mycorrhizae. The individual effects of VAM and PS (*Pseudomonas* and *Agrobacterium* spp.) appear to be additive for solubilizing P from rock phosphate (Azcon et al., 1976). Under natural conditions effects of PS organisms will depend on how they interact with the general microbial population and how they survive under the prevailing soil environment.

4. *Other techniques.* A number of other techniques have been suggested for increasing the dissolution of rock phosphate when used directly as a source of phosphorus. These include the following:
 - Combining N fertilizers with rock phosphate by banding, granulating, or compacting.
 - Composting with animal manure or organic residues (Mishra et al., 1984).
 - Including fine-rooted legumes in rotation to generate a low-pH rhizosphere with low Ca concentrations (Sharpley et al., 1992).

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